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(54) Corrosion inhibitor

(57) A corrosion-inhibiting composition contains salts of orthophosphoric acid and of a dicarboxylic acid, preferably adipic acid. The components are known individually to be corrosion inhibitors, but it has been found that, due to synergistic effect, they give improved protection against corrosion when used together. The composition is particularly useful in the cooling system of internal combustion engines.

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Fig.1

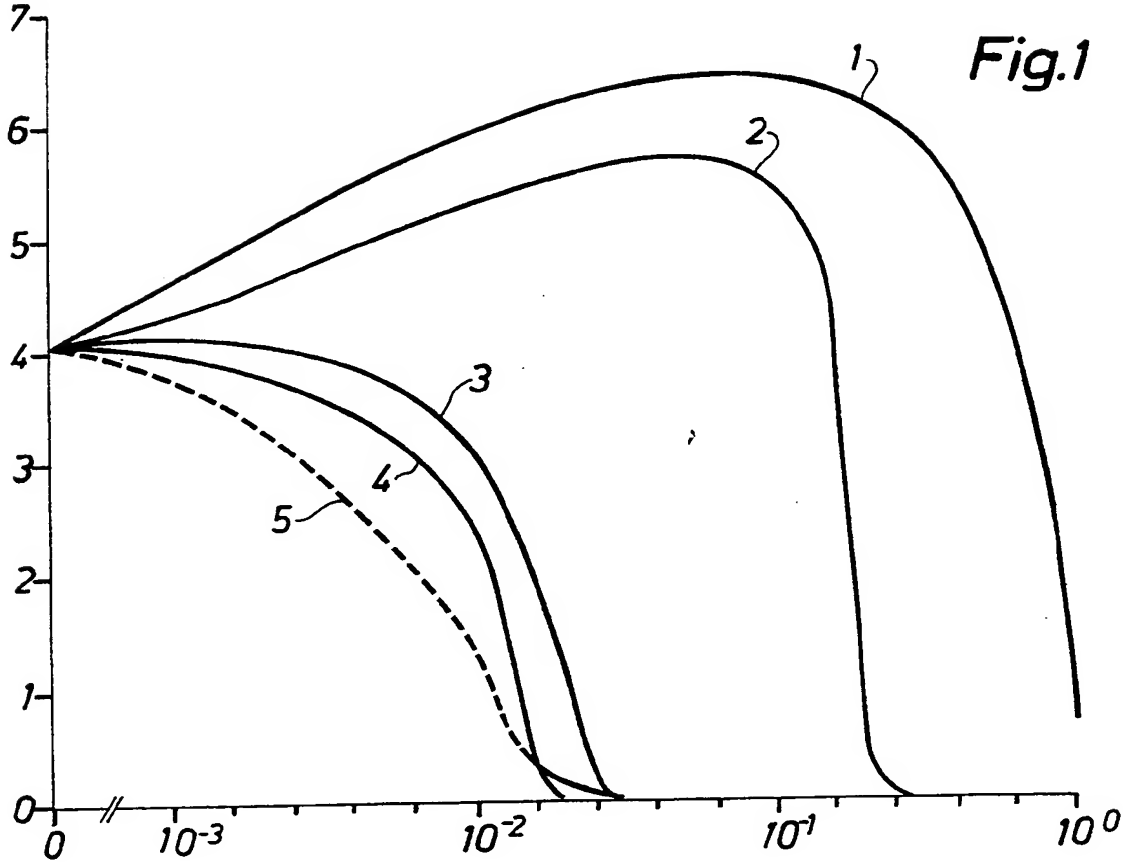
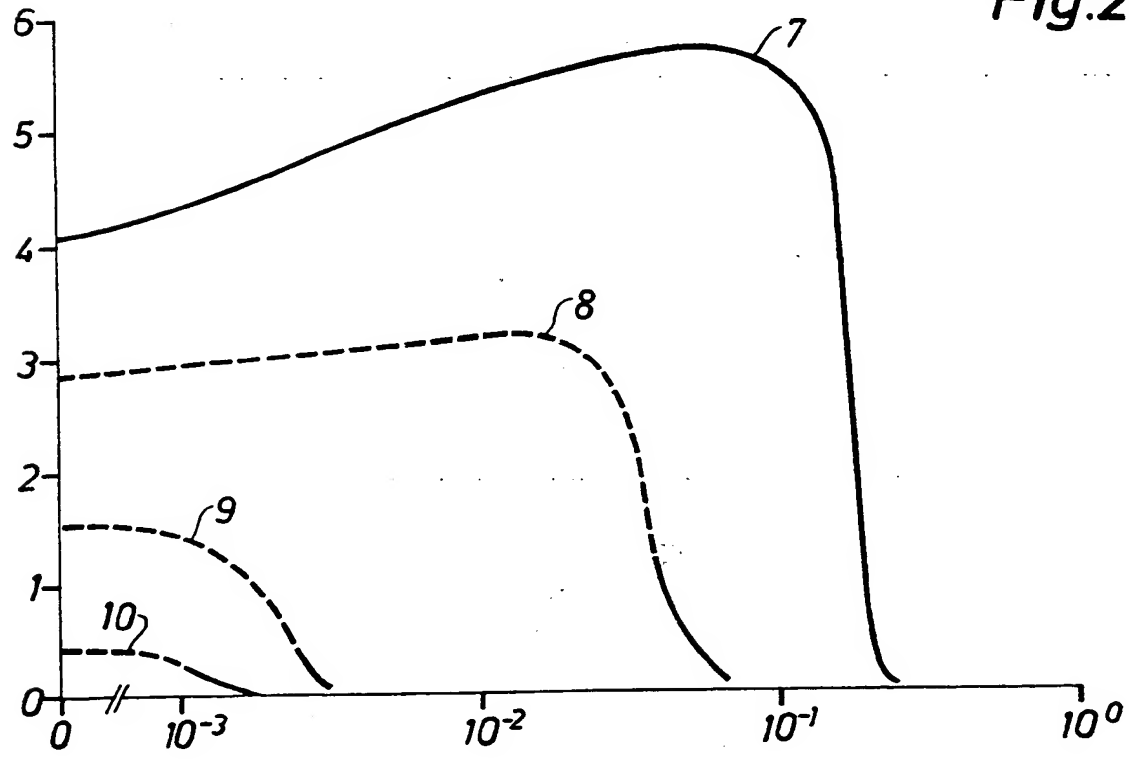


Fig.2



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SPECIFICATION
Corrosion inhibitor

TECHNICAL FIELD:

The present invention relates to a method for treating an aqueous system in order to inhibit the corrosion of cast iron and cast aluminium in contact with the system. A particular object of the invention is to reduce or inhibit the corrosion in the cooling system of an internal combustion engine.

BACKGROUND ART:

Chromates, dichromates, nitrites, silicates, polyphosphates, phosphates, borates, benzoates, etc. have been used for many years to combat corrosion in aqueous heat-transfer liquids. However, many of these inhibitors have serious drawbacks. Chromates and dichromates are toxic. Nitrites can be bacterially decomposed. Silicates have a tendency to cover metal surfaces with a hydrated siliceous gel which may reduce the heat-transfer process. A feature common to inorganic inhibitors is that the concentration must exceed a certain value in order to achieve effective corrosion inhibition. If lower concentrations are used corrosion may instead be accelerated. Too low a concentration usually causes pitting and crevice corrosion, two "dangerous" types of corrosion. The term pitting is used in this specification to define a localized corrosion attack resulting in pits with a small area but often with a considerable depth. The term crevice corrosion is used to define a localized corrosion attack in narrow crevices filled with liquid. The level of concentration must therefore be supervised, which is a drawback. Organic inhibitors, such as benzoates mentioned above, do not suffer from this drawback, but they are required in extremely high doses in order to achieve effective inhibition.

There are special problems to be contended with in inhibiting corrosion in the cooling systems of internal combustion engines. The greatest problem to be solved is to find a corrosion inhibitor or a mixture or corrosion inhibitors which will give an acceptable protection for all the metals and alloys composing the cooling system. These may be cast iron, cast aluminium, steel, copper, brass and soldering tin. Various standard combinations of corrosion inhibitors are available on the market to achieve acceptable protection. A common denominator for these combinations is that the corrosion inhibitors are soluble in ethylene glycol.

This ethylene glycol (or possibly propylene glycol), to which corrosion inhibitors have been added is known as anti-freeze fluid. The anti-freeze fluid is mixed with water to give the coolant ready for use. The ratio of anti-freeze:water is determined by the desired lowering of the freezing point. A normal ratio is 1 part anti-frreze to two parts water. The quantity of corrosion inhibitor in the anti-freeze fluid shall be such that the corrosion protection will be satisfactory in the coolant. All the standard combinations of corrosion inhibitors available today for this purpose have certain disadvantages described below.

The U.S. military specification Mil-E-5559 and corresponding British Standard BS 3150 prescribe a combination of triethanol aminophosphate and sodium mercaptobenzothiazole. The task of the triethanol aminophosphate is to protect cast aluminium, steel and cast iron from corrosion. Since triethanol amine may be corrosive towards copper and its alloys (brass), an inhibitor is required against copper corrosion. Sodium mercaptobenzothiazole is very efficient in this respect. However, this compound is sensitive to oxidation and is now to an increasing extent being replaced by the oxidation-stable compound 1,2,3-benzotriazole or derivates thereof. The most notable feature of these combinations of corrosion inhibitors is that the protection is satisfactory for particularly cast aluminium in accordance with the standards set by motor manufacturers. However, the protection with respect to cast iron does not meet today's requirements.

British specification NS 3151 prescribes a combination of sodium benzoate and sodium nitrite. This combination provides effective protection against corrosion on cast iron and steel. However, it has the disadvantage that the pH value in general increases in a closed cooling system. With the increase in pH value the cast aluminium and soldering tin (in the cooler) are attacked. The combination can be improved by the addition of extra benzotriazole. However, the addition of benzotriazole does not solve the problem of the increased pH value. This means that BS 3151 should be avoided in cooling systems which have aluminium in them. Another drawback with BS 3151 is the high percentage of benzoate required.

The British specification BS 3152 prescribes borax as inhibitor. This inhibitor system does not fulfil today's demands for a corrosion inhibitor. However, combinations of, for instance BS 3150 and BS 3152 are available to be used together with ethylene glycol. When such ethylene glycol is mixed with water an anti-freeze liquid is obtained which has a pH of about 7.5, and which can give a good corrosion protection. The combination of BS 3150 and BS 3152 is not suitable to be used in water alone. The reason is that the resulting pH will be about 9.2, resulting in an unacceptable increase of the corrosion upon aluminium, and also upon soldering tin. The same complication results if an anti-freeze liquid based upon borax is diluted too much. Increased use of aluminium and its alloys in th cooling syst ms of combustion engines therefore advocates against the use of borax.

The aims in the development of an inhibitor system for a water-based cooling and heat-transfer system have therefore been as follows:

1. The inhibitor system shall provide long-term protection for steel, cast-iron and aluminium alloys.

As a consequence, the inhibitors used shall be stable with respect to temperature and oxidation.

2. It shall be possible to combine the inhibitor system with other known inhibitors used in combustion engine cooling systems in order to ensure protection against corrosion of soldering tin, copper and copper alloys such as brass.

3. It shall be possible to use the inhibitor system and its combinations with other known inhibitors both in water and in water mixed with agents for lowering the freezing point, such as glycol.

4. The inhibitor system shall be easily soluble in ethylene glycol and propylene glycol to enable the manufacture of concentrated anti-freeze fluid.

During experiments in endeavouring to realize the aims set out above, aliphatic dicarboxylic acids claimed attention at an early stage. It has long been known that alkali salts of these can protect steel even when used in moderate concentrations. It was therefore reasonable to investigate the corrosion protecting effect on cast iron. It was found that the dicarboxylic acids tested can give increased corrosion if the concentration is below a certain limit value. However, the corrosion is uniformly spread, i.e. there is no pitting or crevice corrosion. If the limit concentration is exceeded complete passivation of cast iron is obtained, i.e. an extremely good corrosion protection. The tested acids and relevant limit concentration in de-ionized water at pH 7.5—7.8 and a temperature of about 22°C were as follows:

Succinic acid	177 g/l
Adipic acid	58 g/l
Azelaic acid	7.5 g/l
Sebacic acid	6.1 g/l

The acids tested are included in the homologous series having the general formula:

$(CH_2)_n(COOH)_2$, where n=2—8

n = 2 succinic acid

n = 3 glutaric acid

n = 4 adipic acid

n = 5 pimelic acid

n = 6 suberic acid

n = 7 azelaic acid

n = 8 sebacic acid

The results obtained show that the acids become more effective the higher the molecular weight. However, high concentrations are required. For this reason succinic acid and adipic acid are not so suitable. While the development work for this invention was in progress, publications have also appeared touching upon the corrosion protecting effect of dicarboxylic acids on cast iron, and these publications support the results above.

DISCLOSURE OF INVENTION:

The method of the invention is characterized in adding to the aqueous system at least one alkali or amine salt of orthophosphoric acid, and at least one alkali or amine salt of either of the dicarboxylic acids having the formula $(CH_2)_n(COOH)_2$, in which n = 3—8, n = 3 being glutaric acid, n = 4 being adipic acid, n = 5 being pimelic acid, n = 6 being suberic acid, n = 7 being azelaic acid, and n = 8 being sebacic acid, the orthophosphoric acid salt being added in a quantity to give the aqueous system a conc ntration of at l ast 1.0 g/l calculated as orthophosphoric acid, and the dicarboxylic acid salt being added in a quantity to give the aqueous system a concentration of at least 0.7 g/l calculated as dicarboxylic acid. The invention is also concerned with a liquid agent for treating an aqueous system with the method of the invention. This agent is characterized in that it consists of an aqueous solution containing

20—30 per cent by weight potassium adipate
15—25 per cent by weight potassium orthophosphate
0—1.5 per cent by weight sodium nitrite

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0—2 per cent by weight benzotriazole
0—0.5 per cent by weight dispersing agent
0—10 per cent by weight ethylene glycol
45—55 per cent by weight water

the molecular ratio potassium:acid being between 1.8:1 and 2:1.

The invention is also concerned with a pulverulent agent for treating an aqueous system with the method of the invention. This agent is characterized in that it consists of a pulverulent mixture containing:

42—62 per cent by weight sodium adipate
23—52 per cent by weight disodium hydrogen orthophosphate
0—4 per cent by weight sodium nitrite
0—6 per cent by weight benzotriazole
0—2 per cent by weight dispersing agent
0—35 per cent by weight water

the molecular ratio sodium:adipic acid being between 1.5:1 and 2:1.

The invention is based upon a surprising and occasionally extremely great synergistic effect which has been established between the aliphatic dicarboxylic acids and orthophosphoric acid. This synergistic effect will now be further revealed.

If orthophosphoric acid (in the following called phosphoric acid) alone is used as corrosion inhibitor under the same conditions as for the organic acids above, a lowest concentration of 4.9 g/l is required to protect cast iron. At lower concentrations pitting and graphitic corrosion occur. If the phosphoric concentration is reduced to 1 g/l or 2 g/l and at the same time one of the organic acids mentioned above is added, the following concentrations of organic acids are required:

	Phosphoric acid	1 g/l	2 g/l
Succinic acid		59 g/l	12 g/l
Adipic acid		0.7 g/l	0.7 g/l
Azelaic acid		0.9 g/l	0.9 g/l
Sebacic acid		1.0 g/l	0.4 g/l

The requisite concentration of organic acid can thus be reduced to considerably below that required when the acid is used alone. The concentrations of organic acid required are only 1/8—1/80 of that required by the acid alone for the protection of cast iron. Adipic acid has the greatest synergistic effect.

The possibility of using a combination of dicarboxylic acid and phosphoric acid as corrosion inhibitor in a combustion engine cooling system has been investigated. Methods were used which have been developed by the American Society for Testing and Materials (ASTM). The methods used are clear from the examples. The ASTM methods use considerably higher temperatures, 71—88°C than in the conditions for the investigation described above. Furthermore, a synthetically corrosive water is used. These more stringent conditions require an increased concentration of inhibitors. During testing the corrosion is determined for cast iron, steel, cast aluminium, soldering tin, copper and brass. All the metals are present simultaneously in the liquid during testing.

Tests performed in glass apparatus showed the following:

1. A combination of adipic acid and sodium nitrite can give a satisfactory protection for all metals. However, a relatively high concentration of adipic acid is required.
2. If the adipic acid is combined with phosphoric acid and sodium nitrite the concentration of adipic acid can be considerably reduced without the corrosion protection diminishing. If benzotriazole is also added, the copper corrosion diminishes, as expected. The corrosion on cast aluminium diminishes at the same time if the concentration of adipic acid and phosphoric acid is increased. It is possible to achieve a protection which fulfills the requirements set for all metals with good margin.
3. If adipic acid or sebacic acid is combined with phosphoric acid and benzotriazole, i.e. no sodium nitrite is included, the corrosion will increase on cast iron and steel. However, the corrosion caused is still well below the requirements stipulated. The corrosion on cast aluminium is negligible. Brass, soldering tin and copper are hardly attacked at all.
4. A corrosion protection according to the invention is obtained with the aid of alkali and/or triethanol amine salts of acids at a pH value between 6.7 and 8.0. The concentration of adipic acid is 3.0—4.3 g/l and of phosphoric acid 2.0—3.0 g/l.

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When testing the corrosion of a coolant in combustion engines the following results were obtained when inhibitors according to the invention were used:

5. A combination of adipic acid, phosphoric acid, benzotriazole and sodium nitrite can give good corrosion protection in a coolant consisting of ethylene glycol and water. In a coolant consisting of only water, however, the pH value tends to increase. This has been measured at 9.8. The corrosion of soldering tin and cast aluminium increases in this case. This applies pariticularly to the corrosion on soldering tin, which becomes totally unacceptable. The reason for the increase in pH value is the presence of sodium nitrite. The presence of this inhibitor in a cooling system in which soldering tin is included, as in the case of a motor vehicle, should therefore be avoided. In aqueous systems without soldering tin, however, this inhibitor combination can be used. One such example is central heating installations.
6. Tests in passenger vehicles and trucks indicate that an inbibitor combination according to the invention can give an almost complete corrosion protection for cast iron and cast aluminium. If adipic acid and phosphoric acid are combined in accordance with the invention and benzotriazole is also added, substantially complete corrosion protection is obtained for all metals and metal alloys used in a cooling system, if the pH is 7.5—8.3. This inhibitor system has shown no tendency to a damaging increase in pH during long-term testing.

The concentration of inhibitors necessary for long-term protection is dependant on the amount of chloride ions in the water used. A high percentage of these requires higher concentrations of inhibitors. The content of phosphoric acid was varied during the tests between 2.0 and 5.4 g/l and the content of adipic acid between 5.8 and 9.3 g/l. The highest contents were used with coolant consisting of corrosive water with 100 mg/l chloride ions. After long-term testing in accordance with the above, the corrosion protection was intact after driving distances of 30,000 km.

7. An inhibitor system according to the invention where the organic acids and phosphoric acid are in the form of potassium and/or triethanol amine salts, can be manufactured in the form of a concentrated solution. This is easily soluble in ethylene glycol. A concentrated anti-freeze fluid containing inhibitors according to the invention can thus be manufactured.

According to the invention it has been ascertained that certain aliphatic dicarboxylic acids, together with phosphoric acid, have a strong synergistic effect as corrosion inhibitors for cast iron in de-ionized water at room temperature. Experiments at higher temperatures, 71°C—88°C, and using a strongly corrosive water have shown that the synergistic effect remains with the use of dicarboxylic acids. It has also been ascertained that the corrosion protection for aluminium is effective. The synergistic effect is obtained when the acids according to the invention are added to an aqueous system in the form of alkali and/or triethanol amine salts. The use of an amine salt other than triethanol amine salt also lies within the scope of the invention.

A corrosion protection according to the invention is obtained when the acids used in the aqueous system give a pH value between 6.7 and 9.8. However, the pH value should preferably be between 7.0 and 8.3.

The organic acid shall consist of the higher dicarboxylic acids (n — 3—8 according to the above formula). The combined concentration of these acids shall be at least 0.7 g/l. The concentration of the phosphoric acid shall be at least 1.0 g/l.

The inhibitor combination according to the invention has been found to be combinable with any one or several of the following known additives for aqueous systems:

a) alkali nitrite to increase the protection of cast iron
b) benzotriazole to inhibit copper corrosion
c) polyacrylates for the dispersion and sequestration of the water hardeners, thus preventing the precipitation of low solubility phosphates.

It also lies within the scope of the invention to combine the inhibitor combination with other inhibitors against copper corrosion. Such inhibitors are, for instance, benzotriazole derivatives such as tolyl triazole, and mercaptobenzothiazole. Also within the scope of the invention is that precipitation of low solubility phosphates can be prevented by additives other than polyacrylates according to the above. Such additives may be polyphosphates, organic phosphonic acids such as aminotri(methyl phosphonic acid) (AMP) and 1-hydroxyethyl-1,1-di-phosphonic acid (HEDP). Also organic chelating agents can be used, such as nitrilotriacetic acid (NTA) and ethylene diamine-tetracetic acid (EDTA). If the aqueous system consists of a coolant in a combustion engine, the best combined corrosion protection is obtained for all the metals and alloys in the cooling system when the pH value is between 6.7 and 8.3. If the organic acid according to the invention consists of adipic acid the following quantities of inhibitors and additives should be added to the coolant:

Adipic acid	3.0—9.3 g/l
Phosphoric acid	2.0—5.8 g/l
Sodium nitrite	0—0.7 g/l

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Benzotriazole	0—0.8 g/l
Dispersing agent	0—0.4 g/l

These inhibitors can be added to the coolant in the form of a concentrated mixture. The mixture may be a concentrated liquid solution containing the potassium or amine salts for the acids. Alternatively, the mixture may be a concentrated powder containing the sodium salts of the acids.

The invention is further illustrated by the following Examples 1—8. The test methods used in the Examples for appraising a coolant from the corrosion point of view have been generally developed by the American Society for Testing and Materials (ASTM). The test methods can be found in the 1965 Annual Book of ASTM Standards, part 22, and the 1975 Annual Book of ASTM Standards, part 30.

EXAMPLE 1

Immersion testing was performed to determine the corrosion protecting influence on cast iron of various aliphatic dicarboxylic acids in combination with orthophosphoric acid. The sodium salts of the acids were used with a pH value of 7.5—7.8.

The following stock solutions were prepared by neutralization of the acids with sodium hydroxide. The balance between base and acid was chosen so that the pH value was 7.5—7.8.

1. Succinic acid	1.0 M
2. Adipic acid	0.5 M
3. Azelaic acid	0.1 M
4. Sebacic acid	0.1 M
5. Orthophosphoric acid	0.1 M

Starting with the above basic solutions, arbitrary lower concentrations of the acids can be prepared, either on their own or in combination with phosphoric acid by diluting with de-ionized water.

The test pieces of cast iron used for testing were of the type used in the following examples for testing according to various ASTM methods.

Testing was performed in the following manner: 100 ml of the test solution was poured into a 150 ml glass beaker. The solution is saturated with air. A cleaned and weighed test piece of cast iron was immersed in the test solution and placed with one short side on the bottom of the beaker. The other short side of the test piece was resting against the side of the beaker. The whole test piece was covered by the solution. The temperature of the test solution was approximately 22°C (room temperature). After 3 days (72 hours) the test piece was removed. It was then inspected, cleaned and weighed. The weight loss was determined in the manner for testing according to ASTM D 1384—62T. The corrosion is specified in this example in mg/24 hours.

The result of the tests are clear from Figs 1 and 2 and Tables 1 and 2.

Fig. 1 illustrates the corrosion on cast iron of various dicarboxylic acids alone, and of orthophosphoric acid alone. Curve 1 relates to succinic acid, curve 2 to adipic acid, curve 3 to azelaic acid, curve 4 to sebacic acid, and curve 5 to orthophosphoric acid. The abscissa represents the concentration of the acids as moles per liter, and the ordinate represents the corrosion as milligrams per 24 hours.

Fig. 2 illustrates the corrosion resulting from the combined effect of adipic acid and orthophosphoric acid in various concentrations. Curve 7 represents adipic acid alone, meaning that curve 7 is identical with curve 2 in Fig. 1. Curve 8 represents an orthophosphoric acid concentration of 5.10^{-3} mole per liter. Curve 9 represents an orthophosphoric acid concentration of 1.10^{-2} mole per liter. Curve 10 represents an orthosphosphoric acid concentration of 2.10^{-2} mole per liter. The abscissa represents the concentration of adipic acid, as moles per liter. The ordinate represents the corrosion as milligrams per 24 hours.

In both Figures the full lines represent a uniform corrosion, and the dashed lines represent pitting and crevice corrosion.

It is clear from Fig. 1 that each of th organic acids tested can give complete corrosion inhibition on its own if the concentration xceeds a certain limit value. The corrosion protection increases with increased molecular weight. The limit concentration for succinic acid about 1.5 M (Mole per liter), whereas it is only 0.03 M for sebacic acid. The corresponding limit concentration for phosphoric acid is 0.05 M. At concentrations below the limit, uniformly spread corrosion was obtained for the organic acids. The corrosion product her is loosely adhered f rric hydrate, which is easily rinsed off. The surface of the metal app ars to be unaffected. With phosphoric acid, the corrosion protection is in the form of an adh r nt phosphate film. If the concentration is below the limit for complete protection there is a dangerous type of corrosion attack. The test piece was attached pointwise and crevice corrosion

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appeared. Graphitic corrosion of the test piece also appeared. With the use of phosphoric acid below the limit concentration, the corrosion attack was coupled with an increased pH value.

Table 1 shows the corrosion inhibition obtained with the organic acids combined with phosphoric acid. The phosphoric acid concentration was constant, 0.01 M and 0.02 M, with varying concentrations of the organic acids. In relation to the limit concentration which is obtained when testing the individual acids according to Fig. 1, a reduction in the limit concentration for the organic acids is obtained here which is sometimes quite drastic.

Table 2 shows the lowest concentrations of various acids required to eliminate corrosion on cast iron. These have been compiled for each of the various organic acids and phosphoric acid when only one of the acids is used, and also for the organic acids in combination with phosphoric acid at the concentrations 0.01 M and 0.02 M. The information is taken from Fig. 1 and Table 1.

The results in this Example shows the following:

1. For corrosion protection of cast iron with phosphoric acid a minimum concentration of 0.05 M (4.9 g/l) is required.
2. If the concentration of phosphoric acid is reduced to 0.01 M (0.98 g/l) and at the same time the phosphoric acid is combined with the aliphatic dicarboxylic acids—succinic, adipic, azelaic and sebacic acid — a good corrosion protection is obtained when the dicarboxylic acid concentration is 1/3—1/80 of the concentration required with the use of the dicarboxylic acids in the absence of phosphoric acid. The lowest effect is obtained with succinic acid and the highest effect with adipic acid. A strong synergistic effect between phosphoric acid and the aliphatic dicarboxylic acids was thus ascertained.
3. If the phosphoric acid concentration is 0.02 M (1.96 g/l), i.e. 2/5 of the lowest concentration required when using phosphoric acid on its own, only 1/15 of the succinic acid concentration is required in comparison with the amount required when using this acid alone. The effect on the other dicarboxylic acids is marginal in comparison with the preceding point 2.
4. Cast iron can be protected from corrosion by a combination of alkali salts of phosphoric acid and the aliphatic dicarboxylic acids mentioned above.
5. The lowest required concentration of phosphoric acid, 0.01 M, coupled with the lowest required concentration of organic carboxylic acids is fulfilled by the adipic acid and its higher homologues. Succinic acid is unsuitable for combination with phosphoric acid at a low concentration of the phosphoric acid. To provide corrosion protection the succinic acid requires an unreasonably high concentration. At a higher concentration of phosphoric acid, 0.02 M, the succinic acid can be used with phosphoric acid, using reasonable concentrations.

From the economic point of view adipic acid and its higher homologues would appear to be suitable to combine with phosphoric acid in order to protect cast iron from corrosion. It is of particular interest to perform further tests on adipic acid together with other corrosion inhibitors in order to determine its suitability as a component in inhibitor combinations intended to provide protection from corrosion for the other metals and metal alloys which may be included in a waterbased cooling and heating system. This is illustrated in the following Examples.

TABLE 1

Corrosion of cast iron in water containing alkali salt or organic dicarboxylic acids in combination with alkali salt of phosphoric acid. The concentration of organic acid varies, while the concentrations of phosphoric acid are constant at 10^{-2} M and 2.10^{-2} M. pH value at the start was 7.5—7.8. Temperature about 22°C.

Phosphoric acid concentration 10^{-2} M
corrosion, mg/24 hours, at various molarity or organic acid

Molarity	10^{-3}	2.10^{-3}	5.10^{-3}	10^{-2}	2.10^{-2}	5.10^{-2}	10^{-1}	5.10^{-1}
Succinic acid				3.2		1.0	0.0	
Adipic acid	1.4	1.2	−0.1	0.2	0.0	0.3	−0.1	
Azelaic acid	1.2	0.3	0.1	0.2				
Sebacic acid	1.0	0.2	0.1	0.0		−0.1		

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TABLE 1 cont'd.

Phosphoric acid concentration 2.10^{-2} M
corrosion, mg/24 hours, at various molarity of organic acid

Molarity	10^{-3}	2.10^{-3}	5.10^{-3}	10^{-2}	2.10^{-2}	5.10^{-2}	10^{-1}	5.10^{-1}
Succinic acid						1.0	0.2	
Adipic acid	0.4	0.1	−0.1	0.2	0.0	0.2		
Azelaic acid	0.4		0.0					
Sebacic acid	0.4	0.0	−0.1		0.1			

Comments:
a) Values underlined with unbroken lines indicate pitting and crevice corrosion
b) Values underlined with broken lines indicate crevice corrosion
c) The accuracy in determining corrosion is ± 0.2 mg/24 hours. If the corrosion values are extremely low, therefore, the figures may be negative (indicate a weight increase).

TABLE 2

The effect of combining an organic dicarboxylic acid with phosphoric acid in order to protect cast iron from corrosion in water at pH 7.5—7.8 and temperature about 22°C. The lowest concentration required to give protection.

	Acid alone	Organic acid + phosphoric acid	
		phosphoric acid = 0.01 M	phosphoric acid = 0.02 M
Succinic acid+/	1.5 M (177 g/l)	0.5 M (59 g/l)	0.1 M (12 g/l)
Adipic acid	0.4 M (58 g/l)	0.005 M (0.7 g/l)	0.005 M (0.7 g/l)
Azelaic acid	0.04 M (7.5 g/l)	0.005 M (0.09 g/l)	0.005 M (0.9 g/l)
Sebacic acid	0.03 M (6.1 g/l)	0.005 M (1.0 g/l)	0.002 M (0.4 g/l)
Phosphoric acid	0.05 M (4.9 g/l)	—	—

+/ The limit concentration for succinic acid alone is stated as 1.5 M. This concentration has been obtained from Figure 1 by means of estimation.

EXAMPLE 2

The suitability of adipic acid, $(CH_2)_4(COOH)_2$ in the form of potassium and/or triethanol amine salt has been tested as corrosion inhibitor according to ASTM D 1384—62T.

The following chemicals were used in preparing the coolants tested:
1) 50 per cent by weight water solution of dipotassium adipate (solution 1)
2) 50 per cent by weight water solution of dipotassium phosphate (solution 2)
3) 50 per cent by weight water solution of triethanol amine phosphate (solution 3)
4) 1,2,3-benzotriazole
5) sodium nitrite
6) ethylene glycol
7) corrosive water in accordance with ASTM D 1384—62T.

Solution 1 was prepared by neutralizing adipic acid with potassium hydroxide and adjusting the concentration to about 50% with distilled water. The balance between acid and base is such that the pH is about 7.7. The adipic acid exists in the solution primarily in the form of the dipotassium salt.

Solution 2 was prepared by dissolving dipotassium phosphate in water and adjusting the pH valu to about 7.7 or about 6.6 with phosphoric acid.

Solution 3 was prepared by neutralizing triethanol amine (TEA) with phosphoric acid in such proportions that the pH value b came about 7.6 or about 7.0.

The pH values stated above refer to diluted water solutions (1 part solution + 50 parts water).

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For the tests the chemicals 1—5 were dissolved in ethylene glycol to provide a corrosion-inhibited anti-freeze fluid. This was then mixed with corrosive water in a ratio by volume of 1:2. The coolant obtained was then tested as to its corrosive properties in accordance with ASTM D 1384—62T.

Coolants according to U.S. specification MIL—E—5559 and British specification B.S. 3150 were used as references during the tests. However, in these references the prescribed inhibitor against copper corrosion, sodium mercaptobenzotriazole, was replaced by the inhibitor 1,2,3-benzotriazole which is more oxidation-stable.

The results obtained are compiled in Table 3 and indicate the following:

1. A combination of adipic acid and sodium nitrite was used as corrosion inhibitor in test 1. The corrosion obtained was well below the stipulate requirements. A relatively high concentration of adipic acid is required.
2. In test 2 the concentration of adipic acid was considerably reduced and at the same time phosphoric acid (the potassium salt) was added. Substantially the same result was obtained as in test 1.
3. In tests 3 and 4 the same inhibitors were used as in test 2, with the addition of benzotriazole. Copper corrosion was also eliminated. The corrosion on cast aluminium and soldering tin also decreased. This was particularly so in test 3 where the concentration of adipic acid and phosphoric acid was increased.
4. In tests 5 and 6 a lower pH value was used than in the preceding tests 3 and 4. The pH value was lowered from 7.7—8.0 to 6.7—7.1. The corrosion decreased on cast aluminium but increased on cast iron and steel. The corrosion on cast iron may approach that permitted at low pH value.
5. In tests 7 and 8 the pH value was raised again to 7.7—7.9. Adipic acid, phosphoric acid and benzotriazole were used as inhibitors. Sodium nitrite has thus been omitted. The corrosion on soldering tin decreased noticeably. Cast iron and steel were subjected more than before to attack, but the corrosion was considerably lower than according to the requirements stipulated. At the same time cast aluminium was effectively protected. In test 8 triethanol amine was used as counter-ion to phosphoric acid (in the solution triethanol amine also exists as counter-ion to adipic acid).
6. Tests 9 and 10 were reference tests according to U.S. specification MIL—E—5559 and British standard 3150, respectively. The corrosion protection was effective for all metals and alloys except steel and cast iron. This applied particularly to cast iron which had an unacceptably high corrosion.

TABLE 3
Testing inhibitor combinations in accordance with ASTM D 1384—62T

Tests 1—8 are in accordance with the invention. Tests 9 and 10 reference tests in accordance with MIL—E—5559 and BS 3150, respectively. The corrosion results are compared with the requirements according to ASTM D 3306—74 and GM 1899—M.

The concentration of corrosion inhibitor in tested coolant is 1/3 of the concentration in anti-freeze fluid.

	g/l in coolant									
Test No.	1	2	3	4	5	6	7	8	9	10
Inhibitors:										
Adipic acid (added as potassium salt)	11	3.0	4.0	4.3	4.0	4.0	3.3	4.0	—	—
Phosphoric acid (added as potassium salt)	—	2.7	3.0	2.0	2.0	3.0	3.0	—	—	—
Triethanol amine (TEA) (added as phosphate	—	—	—	—	—	—	—	7.0	7.0	9.3
Phosphoric acid (added as TEA-salt)	—	—	—	—	—	—	—	2.0	2.0	3.3
Benzotriazole	—	—	0.33	0.17	0.17	0.17	0.33	0.67	0.67	0.67
Sodium nitrite	0.67	0.50	0.50	0.67	0.50	0.50	—	—	—	—
pH at start	7.7	7.7	7.7	7.8	6.9	6.7	7.8	7.7	7.6	7.1
pH at finish	7.8	7.8	7.7	8.0	7.1	7.0	7.9	7.8	7.6	7.0

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Test No.	Weight losses, m/gtest sheet 1	2	3	4	5	6	7	8	9	10	ASTM	GM
Test sheets:												
Cast aluminium	12	10	6	9	2	2	5	2	4	3	30	24
Cast iron	1	1	1	0	4	9	4	4	15	53	10	10
Steel	1	1	1	2	1	3	3	2	5	7	10	9
Brass	0	1	0	0	0	0	0	1	1	1	10	9
Soldering tin	4	6	1	3	2	4	0	1	0	1	30	17
Copper	1	2	0	0	1	0	0	1	1	0	10	9

Comment: Weight losses indicated as zero were less than 0.5 mg/test sheet. Weight losses up to 5 mg/test sheet: accuracy ± 1 mg/test sheet. Higher weight losses: accuracy ± 20%.

EXAMPLE 3

The sodium salts of adipic and sebacic acid were tested as corrosion inhibitors under the same conditions as stated for test 7 in Example 2 (Table 3).

The composition of the coolants tested was as follows:

	g/l in coolant
Test No. 11, adipic acid	3.3 (0.023 M)
Test No. 12, sebacic acid	4.6 (0.023 M)
Also included	
Sodium salt of phosphoric acid, calculated as phosphoric acid	3.0 (0.031 M)
Benzotriazole	0.33

The test results can be seen in Table 4.

TABLE 4

Testing sodium salts of adipic acid (test 11) and sebacid acid test (test 12) in accordance with ASTM D 1384—62T. pH 7.6—7.8.

Test No.	Weight losses, mg/test sheet 11	12
Test sheets		
Cast aluminium	6	5
Cast iron	4	3
Steel	2	2
Brass	0	0
Soldering tin	1	0
Copper	0	0

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Comments:

1. Adipic acid and sebacic acid are equivalent as corrosion inhibitors when combined with phosphoric acid and benzotriazole.
2. The sodium salts of the dicarboxylic acids give equivalent results to those obtained using the potassium salts.
3. Foaming occurs when testing sebacic acid (test 12). This is caused by the air being blown through in accordance with the test method. This was overcome by the addition of a foam-quencher during testing (silicone type).

EXAMPLE 4

An inhibitor composition according to the invention was tested with a modification of the testing method ASTM D 2847—72.

Testing was performed in a straight six-cylinder diesel engine with an output of 296 hp (218 kW). The deviation from ASTM D 2847—72 was as follows:

a) the engine was not installed in a motor vehicle but instead in a motor laboratory. The testing time can thus be shortened as compared to testing in a motor vehicle.
b) all metal packs were removed at the end of the test.
c) the testing period was 39 days. The running time for the engine was 874 hours. The engine has thus been running almost continuously (22.4 h/day).

The tested coolant consisted of corrosive water according to ASTM D 1384—70 to which corrosion inhibitors had been added. The corrosion inhibitors were added to the water in the form of a liquid concentrate.

The concentration of the inhibitors is as follows:

Adipic acid, supplied as potassium salt	9.3 g/l
Phosphoric acid, supplied as potassium salt	5.8 g/l
Benzotriazole	0.75 g/l
Dispersing agent (sodium polyacrylate)	0.20 g/l

The dispersing agent was added to eliminate the effect of hard water. Other complexing agents and dispersing agents may be used; such as organic phosphonic acids and inorganic polyphosphates.

When testing in accordance with the above and the pH value was 7.9 at the start and 8.3 at termination of the test.

The average corrosion loss on the test sheets can be seen in Table 5. By way of comparison, the highest permissible corrosion according to GM 1899—M when testing in simulated cooling systems is indicated.

TABLE 5

Testing inhibitor systems according to the invention in diesel engines in which the coolant consists of corrosive water.

Test method according to modified ASTM D 2847—72

Test sheets	Weight losses on test sheets: Invention	GM 1899—M
Cast aluminium	1.9	3.2
Cast iron	0.3	3.2
Steel	0.2	3.2
Brass	0.1	1.6
Soldering tin	0.2	3.2
Copper	0.2	1.6

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Comment: The weight losses are given as milligrams per 24 hours and square decimeter. Cleaning of the cast aluminium after the test period was too strong and the factual weight loss was less than that stated in the Table. In spite of this the weight loss was well below the limit according to GM 1899—M although this specification prescribes a coolant consisting of 33 vol.% ethylene-glycol and 67 vol.% corrosive water.

EXAMPLE 5

The corrosion protection of an inhibitor composition according to the invention was tested substantially in accordance with the stipulations listed in ASTM D 2847—72.

The test was performed in two similar trucks provided with six-cylinder diesel engines with an output of 218 kW (296 hp). In one of the vehicles the coolant consisted of corrosive water according to ASTM D 1384—70. In the other vehicle the coolant consisted of a mixture of ethylene glycol and corrosive water in a volume ratio of 40:60. Inhibitors in accordance with Table 6 were added to the coolants.

TABLE 6

Inhibitors in coolants during testing in accordance with ASTM D 2847—72.

	Truck 1	Truck 2
	Corrosive water	Ethylene glycol: corrosive water, 40:60
Adipic acid (added as potassium salt)	8.6 g/l	7.1 g/l
Phosphoric acid (added as potassium salt)	5.4 g/l	4.4 g/l
Bensotriazol	0.77 g/l	0.63 g/l
Dispersing agent	0.15 g/l	1.12 g/l

The metal sheets used for the test had not exactly the same composition as according to ASTM D 1384—70. The composition was adjusted in accordance with the motor manufacturer's wishes and can be seen in Table 7.

TABLE 7

Test sheets used for testing in accordance with ASTM D 2847—72

Cast aluminium A	according to SIS 4251 (containing copper)
Cast aluminium B	according to SIS 4253
Cast iron	according to Scania 51492
Brass	according to SIS 2152—04
Soldering tin	with 62.3% lead; 35.8% tin; 1.9% antimony
Copper	according to SIS 5015—02.

Comment: The corrosion on steel was not determined since this has lower corrosion than cast iron. In the "non-precious" part of the metal pack there was therefore place for two types of cast aluminium.

The corrosion losses on the test sheets inserted in the cooling systems of the trucks as specified were determined during running intervals of about 5000 km over the entire distance driven which constituted approximately 30,000 km. The corrosion losses were also determined for sh ts inserted in the cooling system during both the first and the second half of the whole distance driven (int rval approx. 15,000 km). One test pack was subjected to corrosion throughout the distance driven (interval approx. 30,000 km). The part-intervals were ther for short r than according to the original method which prescribes 5000 miles (8,047 km). On the other hand, the total test distance, about 30,000 km, is shorter than according to th original method which prescribes 25,000 miles (40,235 km).

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The test results are compiled in Tables 8 and 9.

TABLE 8
Testing according to ASTM D 2847—72 in truck.
Coolant: corrosive water with the addition of inhibitors according to Table 6 (vehicle 1)

Distance driven, km									
Total after start	0	5217	10159	14789	14789	20860	30022	30022	30022
Interval	0	5217	4942	4630	14789	6071	9162	15233	30022
Testing period, 24-hour periods									
Total	0	23	82	111	111	173	238	238	238
Interval	0	23	59	29	111	62	65	127	238
Weight losses									
g/m² per 5000 km									
Cast aluminium A	—	11.3	12.3	15.6	7.1	9.7	15.6	9.8	4.1
Cast aluminium B	—	7.7	9.3	11.0	5.7	8.7	12.1	7.4	3.0
Cast iron	—	8.5	6.4	5.2	4.0	2.6	5.4	1.6	2.9
Brass	—	0.2	0.2	0.2	0.2	0.4	0.6	0.5	0.4
Soldering tin	—	3.3	2.3	1.6	3.0	1.8	1.3	1.7	1.5
Copper	—	0.2	0.2	0.2	0.1	0.3	0.3	0.3	0.2
Analysis									
pH	7.7	7.7	7.7	7.7	7.7	8.1	7.8	7.8	7.8
Reserve alkalinity, ml	13.0	12.6	12.0	11.0[+/]	14.0				13.5
Adipic acid, g/l	8.6		6.5	8.4					8.0
Phosphoric acid, g/l	5.4		4.1	5.2					4.9
Benzotriazole, g/l	0.77		0.52	0.66					0.64

[+/] The "reserve alkalinity" indicates the consumption of ml 0.1 M hydrochloric acid to reduce the pH value to 4.5 in a sample of 20 ml. Due to a slight leak the concentration of inhibitor was adjusted after a trial period of 111 days (14,789 km).

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TABLE 9

Testing in accordance with ASTM D 2847—72 in truck.
Coolant: 40 per cent by volume ethylene glycol, 60 per cent by volume corrosive water. Inhibitors added according to Table 6 (vehicle 2)

Distance driven, km										
Total after start	0	4669	10173	15168	15168	19933	24669	30075	30075	30075
Interval	0	4669	5504	4995	15168	4765	4736	5406	14907	30075
Testing period, 24-hour periods										
Total	0	54	82	112	112	202	236	278	278	278
Interval	0	54	28	30	112	90	34	42	166	278
Weight losses										
g/m² per 5000 km										
Cast aluminium A	—	0.8	0.8	0.8	0.4	0.7	1.4	1.6	1.1	1.1
Cast aluminium B	—	0.2	0.5	1.0	0.2	1.1	1.1	1.2	0.6	0.2
Cast iron	—	2.7	2.1	2.0	1.2	2.4	3.0	1.0	1.4	1.6
Brass	—	0.2	0.2	0.4	0.1	0.8	0.8	0.7	0.5	0.4
Soldering tin	—	0.9	0.8	1.1	0.4	1.4	1.1	2.6	1.5	1.0
Copper	—	0.3	0.2	0.2	0.1	0.5	0.6	0.5	0.5	0.2
Analysis										
pH	7.7	7.6	7.6	7.6	7.6	7.6	7.6	7.5	7.5	7.5
Reserve alkalinity, ml	10.5	10.5	9.0	8.5→10.0+/			9.5			
Adipic acid, g/l	7.1			5.6	6.7					
Phosphoric acid, g/l	4.4			3.6	4.2					3.2
Benzotriazole, g/l	0.63			0.44	0.54					0.35

+/ after a trial period of 112 days (15,168 km) the reserve alkilinity was adjusted up to 10.0 ml by the addition of inhibitors to compensate for losses.

As is clear from Tables 8 and 9 the corrosion has been calculated as g/m² per 5000 km. In cases where the distance driven differed the corrosion measured has been calculated in g/m² proportionally to 5000 km. The results indicate that in general the corrosion is lower the longer the driving interval. This is particularly noticeable for the corrosion on cast aluminium and cast iron when testing with corrosive water (Table 8). When testing with a coolant consisting of ethylene glycol + corrosive water (Table 9) the corrosion is on the whole lower for the non-precious metals so the reduced corrosion at longer driving intervals is less noticeable. However, this observation is applicable to cast aluminium B.

The reduction in corrosion at longer driving intervals is probably due to a protective film being formed at the start of the test period. This protective film then reduces the corrosion rate.

Upon inspection of the test sheets no pitting could be detected. The corrosion obtained on test sheets tested over the entire distance driven, 30.000 km, can therefore be used to calculate the corrosion depth n various metals upon long-term employment of a corrosion protection according to the invention. By division of the corrosion, measured in in g/m², by the density of the m tal, measured in

g/cm³, th corrosion depth is obtained in microns (10^{-3} mm). The following densities (rounded off) were used for the metals in this calculation:

Cast aluminium	2.7 g/cm³
Cast iron	7.2 g/cm³
Brass	8.8 g/cm³
Soldering tin	10.8 g/cm³
Copper	8.9 g/cm³

A truck may be estimated to have a driving distance of 250,000 km/year when used intensively. The annual corrosion may then be expected to be 50 times greater than that measured after a test interval of 30,000 km and reported as g/m² per 5000 km in Tables 8 and 9. By multiplication of these corrosion values by a factor of 50 and division by the density of the metals in accordance with the above, the corrosion depth is obtained as compiled in Table 10.

TABLE 10

Corrosion depth of various metals after a driving distance of 250,000 km, corresponding to intensive driving over a one year period.

	Corrosive water	Ethylene glycol: corrosive water 40:60
Cast aluminium A	80 μm	20 μm
Cast aluminium B	60 μm	6 μm
Cast iron	20 μm	11 μm
Brass	1 μm	2 μm
Soldering tin	7 μm	5 μm
Copper	1 μm	1 μm

The results in Table 10 indicate the following:

On the whole, cast aluminium A (containing copper) has more of a tendency to corrode than cast aluminium B. The latter type is therefore to be preferred. However, extremely satisfactory corrosion protection for both types of cast aluminium is obtained in a coolant mixture consisting of ethylene glycol and corrosive water. After 10 years running the corrosion depth can be estimated at 0.2 mm for cast aluminium A and 0.06 mm for cast aluminium B. The corrosion increases noticeably if the coolant consists only of corrosive water, probably partly due to the increased concentration of chloride ions in this case (an increase from 60 to 100 ppm). After 10 years running the corrosion depth can be estimated at 0.6 mm for cast aluminium B. In view of the corrosive environment, this is considered to be a satisfactory result.

Cast iron is protected against corrosion in a satisfactory manner in both cases. The corrosion depth after 10 years running is then 0.2 mm when the coolant consists of corrosive water and 0.1 mm when the coolant consists of a mixture of ethylene glycol and corrosive water.

The corrosion on brass, soldering tin and copper is extremely low in all cases. The highest corrosion is on soldering tin, 7 microns in corrosive water. After 10 years running this corresponds to a corrosion depth of 0.07 mm. This is considered an extremely satisfactory value.

The experim nt describ d in this example indicates that an inhibitor combination according to the invention has the unique property of being able at the same time to provide good corrosion protection for both cast aluminium and cast iron in the cooling system of a motor vehicle. Other metals or metal alloys in a cooling system are at the same time almost completely protected.

EXAMPLE 6

An aqueous, heat-transfer liquid according to the invention can be prepared by dissolving an inhibitor concentrat in the liquid, said concentrate including all necessary corrosion inhibitors and additives. Such a concentrate can be pr pared since, during the development of this invention, it has

been found that potassium and triethanol amine salts of certain dicarboxylic acids are extremely easily dissolved in water. An approximately 50 per cent by weight water solution of dipotassium adipate can thus easily be prepared at about 15°C. The high solubility is already known for the corresponding salts of orthophosphoric acid.

An inhibitor concentrate with a high solubility, the acids being included in the form of potassium salts, may have a composition within the following limits, as per cent by weight:

20 — 30	potassium adipate
15 — 25	potassium orthophosphate
0 — 1.5	sodium nitrite
0 — 2	benzotriazole
0 — 0.5	dispersing agent
0 — 10	ethylene glycol
45 — 55	water

The mole ratio potassium:acid should be from 1.8:1 to 2:1. A heat-transfer liquid to which 20—100 g/l of such a concentrate has been added will have a pH value between 7 and 9.

A concentrate according to the above can be produced by dissolving dipotassium hydrogen phosphate, dipotassium adipate and other desired additives in the solvent. The pH value of the heat-transfer liquid will be about 9. A lower pH value is obtained if the concentrate is provided with orthophosphoric acid and/or adipic acid down to a mole ratio potassium:acid 1.8:1. At this mole ratio the pH value will be about 7.

The inhibitor concentrate is easily dissolved in ethylene glycol and can therefore be used to prepare a corrosion-inhibiting anti-freeze fluid.

EXAMPLE 7

An inhibitor concentrate according to Example 6 is prepared by neutralizing adipic acid and phosphoric acid with potassium hydroxide solution, so that the mole ratio potasssium:acid is 1.89. Such a concentrate givesa pH value of 7.7 in a heat-transfer liquid.

In order to produce 100 parts of inhibitor concentrate, 12.4 parts phosphoric acid solution, having a concentration of 85.0 per cent by weight, and 17.1 parts adipic acid solution, having a concentration of 99.7 per cent by weight, is neutralized with 51.7 parts potassium hydroxide solution having a concentration of 46.0 per cent by weight. Neutralization takes place in a reaction vessel provided with cooling jacket, while being stirred. The temperature increase during neutralization is limited to about 50°C by cooling with cooling water. 1.5 parts benzotriazole (100% concentration) and 0.3 parts sodium polyacrylate (dispersing agent) are also mixed into the reaction mixture, together with 8.6 parts water and 8.4 parts ethylene glycol. A clear solution is obtained after filtering off any impurities (in the benzotriazole).

The inhibitor concentrate obtained has the following composition, in per cent by weight:

25.5 potassium adipate	} mole ratio potassium:acid = 1.89:1
18.3 potassium orthophosphate	
1.5 benzotriazole	
0.3 dispersing agent	
8.4 ethylene glycol	
46.0 water	
100.0	

The percentage of adipic acid and orthophosphoric acid in the concentrat is 17.0 and 10.5%, respectively.

A concentrate according to this example was used to prepare the coolants tested in Example 5. The coolants used can be seen in Table 6. The coolant in truck 1 (corrosive water) can be prepared by mixing 51 g/l of the concentrate in the water. The coolant in truck 2 can be prepared by mixing 9.3 parts

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of concentrate with 90.7 parts of ethylene glycol and then mixing this anti-freeze fluid with corrosive water in the ratio by volume 40:60.

EXAMPLE 8

A pulverulent composition according to the invention is preferably based upon the sodium salts of the phosphoric acid and the dicarboxylic acids. Such a composition was made in this way.

40.2 parts by weight adipic acid, 45.4 parts disodium hydrogen phosphate ($Na_2HPO_4.2H_2O$), 3.4 parts benzotriazole, and 0.7 parts sodium polyacrylate (dispersing agent) were charged into a mixer of the Schaufel type, provided with a heating jacket. The pulverulent ingredients were mixed, and 25 parts water and 49.5 parts sodium hydroxide solution having a concentration of 40 per cent by weight were now added, resulting in a temperature increase to 60°C. The mixture is a thick slurry. The slurry was now heated to 80°C, and air was blown through the slurry, resulting in the slurry being transformed into a dry powder. The resulting product was 100 parts by weight of a dry powder which could readily be dissolved in an anti-freeze liquid. The powder had this composition, in per cent by weight:

51:1 sodium adipate (mole ratio sodium:acid 1.80:1)

36.2 disodium hydrogen phosphate

3.4 benzotriazole

0.7 sodiumpolyacrylate

8.6 water

The weight percentage, calculated as acid, was 40.2 per cent adipic acid and 25.0 orthophosphoric acid. The powder had a concentration of the active components which was about 2.4 times that of the liquid product manufactured according to Example 7.

CLAIMS

1. Method of treating an aqueous system to inhibit the corrosion of cast iron and cast aluminium in contact with the system, comprising adding to the aqueous system at least one alkali metal salt or amine salt of orthophosphoric acid, and at least one alkali metal salt or amine salt of at least one dicarboxylic acid selected from glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid, the orthophosphoric acid salt being added in a quantity to give the aqueous system a concentration of at least 1.0 g/l calculated as orthophosphoric acid, and the dicarboxylic acid salt being added in a quantity to give the aqueous system a concentration of at least 0.7 g/l as dicarboxylic acid..

2. Method according to claim 1, wherein the aqueous system has a pH value of 6.7—9.8, preferably 7.0—8.3.

3. Method according to claim 1 or 2 wherein there is added to the aqueous system at least one of the following additives:

a) Alkali metal nitrite for increased protection of cast iron,

b) Benzotriazole and/or benzotriazole derivative and/or mercaptobenzothiazole in order to reduce copper corrosion,

c) An agent to disperse or prevent precipitation caused by hard water, such as polyacrylates, polyphosphates, organic phosphonic acids, organic chelating agent.

4. Method according to any one of the preceding claims, wherein the dicarboxylic acid is adipic acid.

5. Method according to any one of the preceding claims, for the treatment of an aqueous coolant in an internal combustion engine, which comprises adjusting the pH of the coolant to 6.7—8.3.

6. Method according to claim 5, comprising adding to the coolant quantities of adipate salt and orthophosphate salt, and optionally other inhibitors to give concentrations in the coolant of 3.0—9.3 g/l adipic acid, 2—5.8 g/l phosphoric acid, 0—0.7 g/l sodium nitrite, 0—0.8 g/l benzotriazole and 0—0.4 g/l dispersing agent.

7. Method according to any one of the preceding claims wherein all inhibitors and additives are added to the coolant in the form of a concentrated liquid or pulverulent mixture.

8. Method for treating an aqueous system according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

9. Anti-corrosive agent for addition to an aqueous system comprising an aqueous solution containing:

20—30 per cent by weight potassium adipate
15—25 per cent by weight potassium orthophosphate
0—1.5 per cent by weight sodium nitrite
0—2 per cent by weight benzotriazole

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0—0.5 per cent by weight dispersing agent
0—10 per cent by weight ethyl n glycol
45—55 per cent by weight water

the molecular ratio potassium:acid being between 1.8:1 and 2:1.

10. Anti-corrosive agent for addition to an aqueous system comprising a pulverulent mixture containing:

42—62 per cent by weight sodium adipate
23—52 per cent by weight disodium hydrogen orthophosphate
0—4 per cent by weight sodium nitrite
0—6 per cent by weight benzotriazole
0—2 per cent dispersing agent
0—35 per cent by weight water

the molecular ratio sodium:adipic acid being between 1.5:1 and 2:1.

11. An agent according to claim 9 or 10 substantially as hereinbefore described with reference to any one of the Examples.

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